

215747US

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :
GUIDO SCHMITZ ET AL : ATTN: APPLICATION DIVISION
SERIAL NO: NEW APPLICATION :
FILED: HEREWITH :
FOR: MULTILAYER COMPOSITE :
BASED ON POLYAMIDE/POLYOLEFIN

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits please amend the above-identified application as follows.

IN THE SPECIFICATION

Page 2, paragraph beginning at line 14 to line 15, amend as follows:

This and other objects have been achieved by the present invention, the first embodiment of which includes a multilayer composite, comprising

Page 4, paragraph beginning at line 7 to line 8, amend as follows:

c) from 69.9 to 0 parts by volume of an unfunctionalized polyolefin,
wherein the sum of the parts by volume of a), b) and c) is 100.

Page 5, paragraph beginning at line 23 to page 6, line 1, amend as follows:

The amount of the polyamide α) in component a) of layer II is preferably 0.1 to 25% by weight. The amount of polyamide α) includes all values and subvalues therebetween, especially including 0.5, 1, 2, 3, 5, 10, 15 and 20% by weight.

Page 6, paragraph beginning at line 2 to page 6, line 11, amend as follows:

Preferred polyamides for the layer I or the bonding agent are first and foremost aliphatic homopolycondensates and copolycondensates, for example PA 46, PA 66, PA 68, PA 612, PA 88, PA 810, PA 1010, PA 1012, PA 1212, PA 6, PA 7, PA 8, PA 9, PA 10, PA 11 and PA 12. The designation of the polyamides corresponds to the international standard, where the first digit(s) indicates the number of carbon atoms in the starting diamine and the last digit(s) indicates the number of carbon atoms of the dicarboxylic acid. If only one number is given, this means that the polyamide has been prepared from an α,ω -aminocarboxylic acid or from the lactam derived therefrom. For further information, reference may be made to H. Domininghaus, Die Kunststoffe und ihre Eigenschaften, pages 272 ff., VDI-Verlag, 1976.

Page 6, paragraph beginning at line 21 to page 7, line 3, amend as follows:

Further preferred polyamides are mixed aliphatic/aromatic polycondensates as are described, for example, in U.S. 2,071,250, U.S. 2,071,251, U.S. 2,130,523, U.S. 2,130,948, U.S. 2,241,322, U.S. 2,312,966, U.S. 2,512,606 and U.S. 3,393,210 and also in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd edition, Vol. 18, pages 328 ff. and 435 ff., Wiley & Sons, 1982. Other preferred polyamides are poly(ether ester amides) or poly(ether amides). Such products are described, for example, in DE-A 25 23 991, DE-A 27 12 987 and DE-A 30 06 961.

Page 7, paragraph beginning a line 15 to line 23, amend as follows:

The polyolefin of layer III or of the bonding agent is, for example, polyethylene or polypropylene. It is in principle possible to use any commercial type of polyolefin. Thus, for example, possible polyolefins are: linear polyethylene of high, intermediate or low density, LDPE, isotactic or atactic homopolypropylene, random copolymers of propene with ethene

and/or 1-butene, ethylene-propylene block copolymers and the like. The polyolefin can further comprise an impact-toughening component such as EPM or EPDM rubber or SEBS. Furthermore, the customary auxiliaries and additives may also be present. The polyolefin can be prepared by any known process, for example by the Ziegler-Natta process, by the Phillips process, by means of metallocenes or by a free-radical process.

Page 9, paragraph beginning at line 2 to page 10, line 2, amend as follows:

As polyamine, it is possible to use, for example, substances from the following classes:

- polyvinylamines (Römpp Chemie Lexikon, 9th edition, Volume 6, page 4921, Georg Thieme Verlag, Stuttgart 1992);
- polyamines which are prepared from alternating polyketones (DE-A 196 54 058);
- dendrimers such as

$$((\text{H}_2\text{N}-(\text{CH}_2)_3)_2\text{N}-(\text{CH}_2)_3)_2-\text{N}(\text{CH}_2)_2-\text{N}((\text{CR}_2)_2-\text{N}((\text{CH}_2)_3-\text{NH}_2)_2)_2$$
 (DE-A-196 54 179) or
 tris(2-aminoethyl)amine, N,N-bis(2-aminoethyl)-N',N'-bis[2-[bis(2-aminoethyl)amino] ethyl]-1,2-ethanediamine,
 3,15-bis(2-aminoethyl)-6,12-bis[2-[bis(2-aminoethyl)amino]ethyl]-9[bis[2-bis(2-aminoethyl)amino]ethyl]amino]ethyl]-3,6,9,12,15-pentaazaheptadecane-1,17-diamine (J.M. Warakowski, Chem, Mat. 1992, 4, 1000-1004);
- linear polyethylenimines which can be prepared by polymerization of 4,5-dihydro-1,3-oxazoles and subsequent hydrolysis (Houben Weyl, Methoden

der Organischen Chemie, Volume E20, pages 1482- 1487, Georg Thieme Verlag, Stuttgart, 1987);

- branched polyethylenimines which are obtainable by polymerization of amidines (Houben-Weyl, Methoden der Organischen Chemie, Volume E20, pages 1482-1487, Georg Thieme Verlag, Stuttgart, 1987) and generally have the following amino group distribution:

from 25 to 46% of primary amino groups,

from 30 to 45% of secondary amino groups and

from 16 to 40% of tertiary amino groups.

Page 10, paragraph beginning at line 12 to line 22, amend as follows:

Examples of combinations of diamine and dicarboxylic acid are

hexamethylenediamine/adipic acid, hexamethylenediamine/dodecanedioic acid, octamethylenediamine/sebacic acid, decamethylenediamine/sebacic acid, decamethylenediamine/dodecanedioic acid, dodecamethylenediamine/dodecanedioic acid and dodecamethylenediamine/2,6-naphthalenedicarboxylic acid. However, it is also possible to use all other combinations, for example decamethylenediamine/dodecanedioic acid/terephthalic acid, hexamethylenediamine/adipic acid/terephthalic acid, hexamethylenediamine/adipic acid/caprolactam, decamethylenediamine/dodecanedioic acid/ ω -aminoundecanoic acid, decamethylenediamine/dodecanedioic acid/lauro lactam, decamethylenediamine/terephthalic acid/lauro lactam or dodecamethylenediamine/2,6-naphthalenedicarboxylic acid/lauro lactam.

Page 11, paragraph beginning at line 20 to page 12, line 9, amend as follows:

In addition, aliphatic, alicyclic, aromatic, araliphatic and/or alkylaryl-substituted monocarboxylic acids having from 3 to 50 carbon atoms, e.g. lauric acid, unsaturated fatty

acids, acrylic acid or benzoic acid, can, if desired, be used as regulators. These regulators enable the concentration of amino groups to be reduced without altering the molecular structure. Furthermore, functional groups such as double or triple bonds, etc., can be introduced in this way. However, it is desirable for the polyamine-polyamide copolymer to have a substantial proportion of amino groups. The amino group concentration of the copolymer is preferably in the range from 150 to 1500 mmol/kg, particularly preferably in the range from 250 to 1300 mmol/kg and very particularly preferably in the range from 300 to 1100 mmol/kg. The amino group concentration of the copolymer includes all values and subvalues therebetween, especially including 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300 and 1400 mmol/kg. Here and in the following, the term: amino groups refers not only to terminal amino groups but also to any secondary or tertiary amine functions present in the polyamine.

Page 14, paragraph beginning at line 9 to line 14, amend as follows:

Impact-toughening rubbers for polyamide molding compositions contain functional groups derived from unsaturated functional compounds which are either copolymerized into the main chain or are grafted onto the main chain. Most useful is EPM or EPDM rubber onto which maleic anhydride has been grafted by a free-radical mechanism. Such rubbers can also be used together with an unfunctionalized polyolefin such as isotactic polypropylene, as described in EP-A-0683210.

Page 15, paragraph beginning at line 24 to page 16, line 8, amend as follows:

When the multilayer composite of the invention is used for conveying or supplying combustible liquids, gases or dusts, e.g. fuel or fuel vapor, it is advisable to make one of the layers of the composite or an additional interior layer electrically conductive. This can be achieved by compounding with an electrically conductive additive by means of all methods

of the prior art. As conductive additive, it is possible to use, for example, conductive carbon black, metal flakes, metal powder, metallized glass spheres, metallized glass fibers, metal fibers (for example of stainless steel), metallized whiskers, carbon fibers (including metallized carbon fibers), intrinsically conductive polymers, e.g. polyaniline, or graphite fibrils. Mixtures of various conductive additives can also be used.

Page 16, paragraph beginning at line 9 to line 12, amend as follows:

The electrically conductive layer is preferably in direct contact with the medium to be conveyed or stored and has a surface resistance of not more than $10^9 \Omega/\text{square}$, preferably not more than $10^6 \Omega/\text{square}$. The method of determining the resistance of multilayer pipes is described in SAE J 2280 (November 1996, paragraph 7.9).

Page 17, paragraph beginning at line 12 to line 21, amend as follows:

4.78 kg of laurolactam were melted at from 180 to 210°C in a melting vessel and transferred to a pressure-rated polycondensation vessel 250 ml of water and 57 ppm of hypophosphorous acid were then added. The cleavage of the laurolactam was carried out at 280°C under autogenous pressure. The vessel was subsequently depressurized over a period of 3 hours to the vapor pressure of residual water of 3 bar and 230 g of polyethylenimine (LUPASOL ® 100, BASF AG, Ludwigshafen) were added. The mixture was then depressurized to atmospheric pressure and polycondensation was carried out at 250°C for 2 hours while passing nitrogen over the reaction mixture. The clear melt was discharged as an extruded strand by means of a melt pump, cooled in a water bath and subsequently granulated.

Page 18, paragraph beginning at line 2 to line 8, amend as follows:

45 parts by weight of VESTAMID® ZA7295 (a high-viscosity PA12 for extrusion molding compositions containing an excess of terminal amino groups), 40 parts by weight of

NOVOLEN® 2500H (an ethylene-propylene block copolymer from Targor GmbH; extrusion grade), 10 parts by weight of ADMER® QB520E (an isotactic polypropylene grafted with maleic anhydride from Mitsui) and 5 parts by weight of the polyamine-polyamide copolymer prepared above were melted and mixed at 250°C for 5 minutes in a laboratory kneader from Haake.

IN THE CLAIMS

Please amend Claims 19 and 21 as follows.

19. (Amended) The multilayer composite as claimed in Claim 1, which is in the form of a fuel line, a tank filling port, a vapor line, a filling station pipe, a coolant line, a pipe in an air conditioning unit, a line for clutch fluid, an air brake line, a windscreen washer pipe or a fuel container.

21. (Amended) A molding composition, comprising:

at least 50% by weight of the following components:

- a) from 30 to 70 parts by volume of a polymer selected from the group consisting of a polyamide, at least 0.1 part by volume of polyamine-polyamide copolymer and a combination of a polyamide and at least 0.1 part by volume of polyamine-polyamide copolymer;

wherein said polyamine-polyamide copolymer is prepared using the following monomers:

- α) from 0.1 to 25% by weight, based on the polyamine-polyamide copolymer, of a polyamine containing at least 3 nitrogen atoms, and

- β) a polyamide-forming monomer selected from the group consisting of a lactam; a ω-aminocarboxylic acid; an equimolar combination of a diamine and a dicarboxylic acid; and a mixture thereof,
- b) from 0.1 to 70 parts by volume of an olefin polymer containing a functional group,
- c) from 69.9 to 0 parts by volume of an unfunctionalized polyolefin,
- wherein the sum of the parts by volume of a), b) and c) is 100.

REMARKS

The specification and Claims 19 and 21 have been amended to correct minor typographical errors and to recite proper language. The amendments are further supported by the German priority application, 100 65 177.1, filed December 23, 2000.

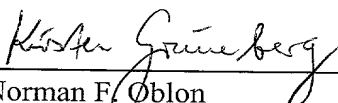
No new matter is believed to have been added by entry of this amendment. Entry and favorable reconsideration are respectfully requested.

Upon entry of this amendment Claims 1-21 will now be active in this application.

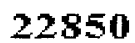
Applicants submit that the present application is now in condition for examination on the merits and early notice of such action is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
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Marked-Up Copy

Serial No: _____

Amendment Filed on: _____

December 26, 2001

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 3,15-bis(2-aminoethyl)-6,12-bis[2-[bis(2-aminoethyl)amino]ethyl]-9[bis[2-bis(2-aminoethyl)amino]ethyl]amino]ethyl]-3,6,9,12,15-pentaazaheptadecane-1,17-diamine (J.M. Warakowski, Chem, Mat. 1992, 4, 1000-1004);
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- branched polyethylenimines which are obtainable by polymerization of amidines (Houben-Weyl, Methoden der Organischen Chemie, Volume E20, pages 1482-1487, Georg Thieme Verlag, Stuttgart, 1987) and generally have the following amino group distribution:
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Page 11, paragraph beginning at line 20 to page 12, line 9, amend as follows:

In addition, aliphatic, alicyclic, aromatic, araliphatic and/or alkylaryl-substituted monocarboxylic acids having from 3 to 50 carbon atoms, e.g. lauric acid, unsaturated fatty acids, acrylic acid or benzoic acid, can, if desired, be used as regulators. These regulators enable the concentration of amino groups to be reduced without altering the molecular structure. Furthermore, functional groups such as double or triple bonds, etc., can be introduced in this way. However, it is desirable for the [polyaminepolyamide] polyamine-polyamide copolymer to have a substantial proportion of amino groups. The amino group concentration of the copolymer is preferably in the range from 150 to 1500 mmol/kg, particularly preferably in the range from 250 to 1300 mmol/kg and very particularly

preferably in the range from 300 to 1100 mmol/kg. The amino group concentration of the copolymer includes all values and subvalues therebetween, especially including 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300 and 1400 mmol/kg. Here and in the following, the term: amino groups refers not only to terminal amino groups but also to any secondary or tertiary amine functions present in the polyamine.

Page 14, paragraph beginning at line 9 to line 14, amend as follows:

Impact-toughening rubbers for polyamide molding compositions contain functional groups derived from unsaturated functional compounds which are either copolymerized into the main chain or are grafted onto the main chain. Most useful is EPM or EPDM rubber onto which maleic anhydride has been grafted by a free-radical mechanism. Such rubbers can also be used together with an unfunctionalized polyolefin such as isotactic polypropylene, as described in [EP-A-0 6883 290] EP-A-0683210.

Page 15, paragraph beginning at line 24 to page 16, line 8, amend as follows:

When the multilayer composite of the invention is used for conveying or [toning] supplying combustible liquids, gases or dusts, e.g. fuel or fuel vapor, it is advisable to make one of the layers of the composite or an additional interior layer electrically conductive. This can be achieved by compounding with an electrically conductive additive by means of all methods of the prior art. As conductive additive, it is possible to use, for example, conductive carbon black, metal flakes, metal powder, metallized glass spheres, metallized glass fibers, metal fibers (for example of stainless steel), metallized whiskers, carbon fibers (including metallized carbon fibers), intrinsically conductive polymers, e.g. polyaniline, or graphite fibrils. Mixtures of various conductive additives can also be used.

Page 16, paragraph beginning at line 9 to line 12, amend as follows:

The electrically conductive layer is preferably in direct contact with the medium to be conveyed or stored and has a surface resistance of not [none] more than 10^9 Ω /square, preferably not more than $[10^9]$ 10^6 Ω /square. The method of determining the resistance of multilayer pipes is described in SAE J 2280 (November 1996, paragraph 7.9).

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IN THE CLAIMS

Please amend Claims 19 and 21 as follows.

--19. (Amended) The multilayer composite as claimed in Claim 1, which is in the form of a fuel line, a tank filling port, a vapor line, a filling station pipe, [a station pipe,] a coolant line, a pipe in an air conditioning unit, a line for clutch fluid, an air brake line, a windscreen washer pipe or a fuel container.

21. (Amended) A molding composition, comprising:
at least 50% by weight of the following components:

- a) from 30 to 70 parts by volume of a polymer selected from the group consisting of a polyamide, at least 0.1 part by volume of polyamine-polyamide copolymer and a combination of a polyamide and at least 0.1 part by volume of polyamine-polyamide copolymer;
wherein said polyamine-polyamide copolymer is prepared using the following monomers:
 - α) from 0.1 to 25% by weight, based on the polyamine-polyamide copolymer, of a polyamine containing at least 3 nitrogen atoms, and
 - β) a polyamide-forming monomer selected from the group consisting of a lactam; a ω-aminocarboxylic acid; an equimolar combination of a diamine and a dicarboxylic acid; and a mixture thereof,
 - b) from 0.1 to 70 parts by volume of an olefin polymer containing a functional group,
 - c) from 69.9 to 0 parts by volume of an unfunctionalized polyolefin,
- wherein the sum of the parts by volume of[,] a), b) and c) is 100.--